Appendix F

Description of the MAGIC Model and Application Methods Employed

Background

The principal tools that can be used to evaluate the potential response of aquatic resources to changes in acidic deposition are mathematical models. One of the prominent models developed to estimate acidification of lakes and streams is MAGIC (Model of Acidification of Groundwater In Catchments, Cosby et al., 1985a-c). MAGIC was the principal model used by the National Acid Precipitation Assessment Program (NAPAP) in assessment of potential future damage to lakes and streams in the eastern United States (NAPAP 1991, Thornton et al. 1990). Most recently MAGIC has been the principal model used for aquatic assessment in the Southern Appalachian Mountain Initiative Assessment activities (Sullivan et al., 2002). The validity of the model has been confirmed by comparison with estimates of lake acidification inferred from paleolimnological reconstructions of historical lake changes in pH (Sullivan et al. 1991, 1996) and with the results of several catchment-scale experimental acidification and de-acidification experiments (e.g., Cosby et al. 1995, 1996). MAGIC has been used to reconstruct the history of acidification and to simulate future trends on a regional basis and in a large number of individual watersheds in both North America and Europe (e.g., Lepisto et al. 1988; Whitehead et al. 1988; Cosby et al. 1990, 1994, 1996; Jenkins et al. 1990; Wright et al. 1990, 1994). Information contained in this Appendix was taken from the model summary provided by Sullivan et al. (2002).

Conceptual Basis of the Model

MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on surface water chemistry. The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in these waters. MAGIC consists of: 1) a section in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving sulfate adsorption, cation exchange, dissolution-precipitation- speciation of aluminum and dissolution-speciation of inorganic carbon; and 2) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering, net uptake and loss to biomass and runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time in response to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change of surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils.

Cation exchange is modeled using equilibrium (Gaines-Thomas) equations with selectivity coefficients for each base cation and aluminum. Sulfate adsorption is represented by a Langmuir isotherm. Aluminum dissolution and precipitation are assumed to be controlled by equilibrium with a solid phase of aluminum trihydroxide. Aluminum speciation is calculated by considering hydrolysis reactions as well as complexation with sulfate and fluoride. Effects of carbon dioxide on pH and on the speciation of inorganic carbon are computed from equilibrium equations. Organic acids are represented in the model as tri-protic analogues. First-order rates are used for retention (uptake) of nitrate and ammonium in the catchment. Weathering rates are assumed to be constant. A set of mass balance equations for base cations and strong acid anions are included. Given a description of the historical deposition at a site, the model equations are solved numerically to give long-term reconstructions of surface water chemistry (for complete details of the model see Cosby et al. 1985 a-c).

Equilibrium Equations
Cation and Anion Exchange in Soil Water

Cation exchange reactions between the soil matrix and soil solution are assumed to result in an equilibrium partitioning of calcium, magnesium, sodium, potassium and trivalent aluminum between solid and aqueous phases. The equilibrium expressions for cation exchange (Table F-1) are constructed using a Gaines-Thomas expression (Gaines and Thomas, 1953). E represents exchangeable fractions of each base cation on the soil (equivalents of each base cation per total cation exchange capacity of the soil). The sum of all exchangeable fractions must equal 1.0. Base saturation of the soil is defined as the sum of the exchangeable fractions of the base cations (Table F-2). The selectivity coefficients (Table F-3) must be calibrated for each aggregated soil layer in the model. The calibration procedure relies on observations of the exchangeable fractions of base cations in soils and measured base cation concentrations in streamwater (see Cosby et al. 1985a,b for details).

Anion exchange reactions are assumed to occur only for sulfate ion. The relationship between dissolved and adsorbed sulfate (Table F-1) is assumed to follow a Langmuir isotherm (Couto et al. 1979, Hasan et al. 1970). MAGIC is a catchment-scale model and it is often the case that the effective values of aggregated parameters intended to represent large-scale function cannot be derived by a direct scaling-up of similar parameters measured in a laboratory setting (see Rastetter et al. 1992). The sulfate adsorption parameters (Table F-3) used in MAGIC must, therefore, be calibrated for each site. Cosby et al. (1986) described the method for calibrating sulfate adsorption parameters in whole catchment simulations based on input/output budgets and deposition histories for the site.

Inorganic Aluminum in Soil Water and Surface Water

Inorganic aluminum speciation consists of one reaction involving the equilibrium dissolution of a solid phase of aluminum trihydroxide and twelve reactions involving formation of aqueous complexes of Al^{3+}. These reactions are assumed to occur both in soil solution and in surface waters in the model and can be represented by a series of equilibrium equations (Table F-1). The aluminum solubility constants for the soils in the model are represented by aggregated values. These values are not, therefore, necessarily associated with a particular crystalline form of $Al(OH)_3$ and must be selected as part of the calibration process.

Inorganic and Organic Carbon in Soil Water and Surface Water; and Dissociation of Water

Inorganic carbon reactions in MAGIC consist of dissolution of CO_2 to form carbonic acid, followed by dissociation to bicarbonate and carbonate. These reactions are assumed to occur both in soil solution and in surface waters in the model and can be represented by equilibrium equations (Table F-1) that are temperature-dependent.

Organic acids are the dominant form of dissolved organic material in natural waters (e.g., McKnight et al. 1985, David and Vance 1991). Organic acids are effective hydrogen ion buffers and can form complexes with inorganic aluminum. Considerable evidence has accumulated suggesting that organic acids influence the response of surface waters to changes in strong acid inputs, most likely by changes in the protonation of the organic acid anions (see Wright 1989). Organic acids were not included in the original formulation of MAGIC because specification (and calibration) of organic acid analog models was hampered by lack of data on organic acid behavior (e.g., Jenkins and Cosby 1989). In 1994, Driscoll et al. (1994) compared several organic acid analog models (mono-, di-, and triprotic organic acid analogs and the model of Oliver et al. 1983) with respect to their abilities to resolve mass balance discrepancies in measured water samples from Adirondack lakes. They concluded that organic acids were

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Table F-1. Equations in the MAGIC model.

Equilibrium Equations

Cation and Anion Exchange in Soil Water

$$E_{Ca} + E_{Mg} + E_{Na} + E_K + E_{Al} = 1.0$$

$$\frac{\{Ca^{2+}\}^3 E_{Al}^2}{\{Al^{3+}\}^2 E_{Ca}^3} = S_{AlCa} \qquad \frac{\{Mg^{2+}\}^3 E_{Al}^2}{\{Al^{3+}\}^2 E_{Mg}^3} = S_{AlMg} \qquad \frac{\{Na^+\}^3 E_{Al}}{\{Al^{3+}\} E_{Na}^3} = S_{AlNa} \qquad \frac{\{K^+\}^3 E_{Al}}{\{Al^{3+}\} E_K^3} = S_{AlK} \qquad \frac{\{SO_4^{2-}\}}{C_{1/2} + \{SO_4^{2-}\}} * E_{mx} = E_{SO4}$$

Inorganic Aluminum in Soil Water and Surface Water

$$\{Al^{3+}\} = [K_{Al}] * \{H^+\}^{S_{Al}}$$

$$\frac{\{Al(OH)^{2+}\}\{H^+\}}{\{Al^{3+}\}} = K_{Al1} \qquad \frac{\{Al(OH)_2^+\}\{H^+\}^2}{\{Al^{3+}\}} = K_{Al2} \qquad \frac{\{Al(OH)_3^0\}\{H^+\}^3}{\{Al^{3+}\}} = K_{Al3} \qquad \frac{\{Al(OH)_4^-\}\{H^+\}^4}{\{Al^{3+}\}} = K_{Al4}$$

$$\frac{\{AlF^{2+}\}}{\{Al^{3+}\}\{F^-\}} = K_{Al5} \qquad \frac{\{AlF_2^+\}}{\{Al^{3+}\}\{F^-\}^2} = K_{Al6} \qquad \frac{\{AlF_3^0\}}{\{Al^{3+}\}\{F^-\}^3} = K_{Al7} \qquad \frac{\{AlF_4^-\}}{\{Al^{3+}\}\{F^-\}^4} = K_{Al8}$$

$$\frac{\{AlF_5^{2-}\}}{\{Al^{3+}\}\{F^-\}^5} = K_{Al9} \qquad \frac{\{AlF_6^{3-}\}}{\{Al^{3+}\}\{F^-\}^6} = K_{Al10} \qquad \frac{\{Al(SO_4)^+\}}{\{Al^{3+}\}\{SO_4^{2-}\}} = K_{Al11} \qquad \frac{\{Al(SO_4)_2^-\}}{\{Al^{3+}\}\{SO_4^{2-}\}^2} = K_{Al12}$$

Inorganic and Organic Carbon in Soil Water and Surface Water; Dissociation of Water

$$\{H^+\}\{OH^-\} = K_w \qquad \frac{\{H_2CO_3^*\}}{P_{CO2}} = K_{CO2_1} \qquad \frac{\{HCO_3^-\}\{H^+\}}{\{H_2CO_3^*\}} = K_{CO2_2} \qquad \frac{\{CO_3^{2-}\}\{H^+\}}{\{HCO_3^-\}} = K_{CO2_3} \qquad \frac{\{H_2A^-\}\{H^+\}}{\{H_3A\}} = K_{OA_1}$$

$$\frac{\{HA^{2-}\}\{H^+\}}{\{H_2A^-\}} = K_{OA_2} \qquad \frac{\{A^{3-}\}\{H^+\}}{\{HA^{2-}\}} = K_{OA_3} \qquad \frac{\{AlA\}}{\{Al^{3+}\}\{A^{3-}\}} = K_{OA_4} \qquad \frac{\{Al(H)A^+\}}{\{Al^{3+}\}\{H^+\}\{A^{3-}\}} = K_{OA_5}$$

Braces denote activities (calculated from concentrations using the extended Debye-Huckel equation)

Mass and Ionic Balance Equations

Ionic Balance in Soil Water and Surface Water (parentheses denote molar concentrations)

$$2(Ca^{2+}) + 2(Mg^{2+}) + (Na^+) + (K^+) + (NH_4^+) + (H^+) + 3(Al^{3+}) + 2(AlOH^{2+}) + (Al(OH)_2^+) + 2(AlF^{2+}) + (AlF_2^+) + (AlSO_4^+) + (Al(H)A^+)$$

$$= 2(SO_4^{2-}) + (Cl^-) + (NO_3^-) + (F^-) + (OH^-) + (HCO_3^-) + 2(CO_3^{2-}) + (H_2A^-) + 2(HA^{2-}) + 3(A^{3-}) + (Al(OH)_4^-) + (AlF_4^-) + 2(AlF_5^{2-})$$

$$+ 3(AlF_6^{3-}) + (Al(SO_4)_2^-)$$

Mass Balance for Ions in Soil Water and Surface Water (rates of change in eq m^{-2} yr^{-1})

$$\frac{dCa_T}{dt} = AD_{Ca} + W_{Ca} + SS_{Ca} - Q*2(Ca^{2+}) \qquad \frac{dNO3_T}{dt} = AD_{NO3} + W_{NO3} + SS_{NO3} + NIT - IM_{NO3} - UP_{NO3} - DEN - Q*(NO_3^-)$$

$$\frac{dMg_T}{dt} = AD_{Mg} + W_{Mg} + SS_{Mg} - Q*2(Mg^{2+}) \qquad \frac{dNH4_T}{dt} = AD_{NH4} + W_{NH4} + SS_{NH4} + MIN - IM_{NH4} - UP_{NH4} - NIT - Q*(NH_4^+)$$

$$\frac{dNa_T}{dt} = AD_{Na} + W_{Na} + SS_{Na} - Q*(Na^+) \qquad \frac{dSO4_T}{dt} = AD_{SO4} + W_{SO4} + SS_{SO4} - Q*2\left[(SO_4^{2-}) + (AlSO_4^+) + 2(Al(SO_4)_2^-)\right]$$

$$\frac{dK_T}{dt} = AD_K + W_K + SS_K - Q*(K^+) \qquad \frac{dCl_T}{dt} = AD_{Cl} + W_{Cl} + SS_{Cl} - Q*(Cl^-)$$

$$\frac{dF_T}{dt} = AD_F + W_F + SS_F - Q*\left[(F^-) + (AlF^{2+}) + 2(AlF_2^+) + 3(AlF_3^0) + 4(AlF_4^-) + 5(AlF_5^{2-}) + 6(AlF_6^{3-})\right]$$

Table F-2. Variables in the MAGIC model.

State Variables   (functions of time, calculated by model)

Aqueous Phase - Ionic Concentrations in Soil Water and Surface Water (mol m^{-3})

Base Cations: $(Ca^{2+})(Mg^{2+})(Na^+)(K^+)(NH_4^+)$ Strong Acid Anions: $(SO_4^{2-})(Cl^-)(NO_3^-)(F^-)$

Hydrogen and Hydroxyl Ions: $(H^+)(OH^-)$ Inorganic Carbon: $(H_2CO_3^*)(HCO_3^-)(CO_3^{2-})$

Aluminum: $(Al^{3+})(AlOH^{2+})(Al(OH)_2^+)(Al(OH)_3^0)(Al(OH)_4^-)(AlF^{2+})(AlF_2^+)(AlF_3^0)(AlF_4^-)(AlF_5^{2-})(AlF_6^{3-})(AlSO_4^+)(Al(SO_4)_2^-)$

Organic Carbon: $(H_3A)(H_2A^-)(HA^{2-})(A^{3-})(AlA)(Al(H)A^+)$

Solid Phase - Exchangeable Ions on Soil Matrix; Soil Organic Matter Constituents

Exchangeable Cations (fraction): $E_{Ca}, E_{Mg}, E_{Na}, E_K, E_{Al}$ Exchangeable Sulphate (eq kg^{-1}): E_{SO4}

Organic Carbon and Nitrogen (mol m^{-2}): C_{Org}, N_{Org}

Defined Variables   (derived from state variables)

Total Ions for Mass Balance (eq m^{-2})

$$SO_{4T} = SM*E_{SO4} + SV*TOT_{SO4}$$

$$Ca_T = SM*CEC*E_{Ca} + SV*2(Ca^{2+}) \qquad Na_T = SM*CEC*E_{Na} + SV*(Na^+) \qquad NO_{3T} = SV*(NO_3^-) \qquad Cl_T = SV*(Cl^-)$$

$$Mg_T = SM*CEC*E_{Mg} + SV*2(Mg^{2+}) \qquad K_T = SM*CEC*E_K + SV*(K^+) \qquad NH_{4T} = SV*(NH_4^+) \qquad F_T = SV*TOT_F$$

Total Aqueous Concentrations (eq m^{-3})

$$SBC = 2(Ca^{2+}) + 2(Mg^{2+}) + (Na^+) + (K^+) \qquad TOT_{Al} = 3(Al)_{TOT} \qquad TOT_F = (AlF^{2+}) + 2(AlF_2^+) + 3(AlF_3^0) + 4(AlF_4^-) + 5(AlF_5^{2-}) + 6(AlF_6^{3-})$$

$$SAA = 2(SO_4^{2-}) + (Cl^-) + (NO_3^-) + (F^-) \qquad DOC_{Al} = 3(Al)_{DOC} \qquad TOT_{SO4} = 2(SO_4^{2-}) + 2(AlSO_4^+) + 4(Al(SO_4)_2^-)$$

Summed Species (mol m^{-3})

$$(Al)_{SO4} = (AlSO_4^+) + (Al(SO_4)_2^-) \qquad (Al)_{DOC} = (AlA) + (Al(H)A^+)$$

$$(Al)_{OH} = (AlOH^{2+}) + (Al(OH)_2^+) + (Al(OH)_3^0) + (Al(OH)_4^-) \qquad (Al)_F = (AlF^{2+}) + (AlF_2^+) + (AlF_3^0) + (AlF_4^-) + (AlF_5^{2-}) + (AlF_6^{3-})$$

$$(Al)_{TOT} = (Al^{3+}) + (Al)_{SO4} + (Al)_{OH} + (Al)_F + (Al)_{DOC} \qquad (OA)_{TOT} = (H_3A) + (H_2A^-) + (HA^{2-}) + (A^{3-}) + (AlA) + (Al(H)A^+)$$

Charge Balance Alkalinity (eq m^{-3}) $CALK = SBC + (NH_4^+) - SAA$ *Soil C/N ratio* $C/N = \dfrac{C_{Org}}{N_{Org}}$

Solution pH, pAl $pH = -\log_{10}(H^+) \qquad pAl = -\log_{10}(Al^{3+})$ *Soil Base Saturation* $BS = E_{Ca} + E_{Mg} + E_{Na} + E_K$

Table F-3. Parameters in the MAGIC model.

Parameters   (constant values that must be specified)

Soil Physical/Chemical Properties

		Surface Water Properties
D = depth (m)	CEC = cation exchange capacity (eq kg^{-1})	RT = retention time (yr)
P = porosity (fraction)	$C_{1/2}$ = sulphate adsorption half saturation (eq m^{-3})	RA = relative area of lake/stream (fraction)
BD = bulk density (kg m^{-3})	E_{mx} = sulphate adosrption maximum (eq kg^{-1})	K_{Al} = aluminum solubility constant (log_{10})
SM = soil mass ($D*BD$)	K_{Al} = aluminum solubility constant (log_{10})	S_{Al} = slope of pH-pAl relationship
SV = soil pore volume ($D*P$)	S_{Al} = slope of pH-pAl relationship	

Aqueous Phase - Equilibrium Constants (log_{10})

Organic Acid: pK_1, pK_2, pK_3 $[\ -log_{10}(K_{OA_1}, K_{OA_2}, K_{OA_3})\ ]$ Organic Aluminum: K_{OA_4}, K_{OA_5}

Inorganic Aluminum Speciation: $K_{Al_1}, K_{Al_2}, K_{Al_3}, K_{Al_4}, K_{Al_5}, K_{Al_6}, K_{Al_7}, K_{Al_8}, K_{Al_9}, K_{Al_{10}}, K_{Al_{11}}, K_{Al_{12}}$

Inorganic Carbon Speciation and Dissociation of Water: $K_{CO_{21}}, K_{CO_{22}}, K_{CO_{23}}, K_w$

Solid Phase - Weathering and Exchange Constants

Cation Exchange Selectivity Coefficients (log_{10}): $S_{AlCa}, S_{AlMg}, S_{AlNa}, S_{AlK}$

Weathering Rates (eq m^{-2} yr^{-1}): $W_{Ca}, W_{Mg}, W_{Na}, W_K, W_{NH4}, W_{SO4}, W_{Cl}, W_{NO3}, W_F$ (can be pH dependent)

important buffers in surface waters even when dissolved organic carbon was low. They obtained the best agreement between predicted and observed pH values using a triprotic organic acid analog model. The triprotic organic acid analog model can also be used to describe the complexation of Al by organic solutes (Schecher and Driscoll 1993, Driscoll et al. 1994). A triprotic organic acid analog model is currently incorporated into the structure of MAGIC.

Mass and Ionic Balance Equations

Mass balance is required for the total amounts of base cations and strong acid anions in each compartment of the simulated watershed (Table F-1). That is, input minus output of each mass balance ion must equal the rate of change of the total amount of that ion in each compartment of the model. Total amounts in surface water compartments are calculated from aqueous concentrations and water volume. In soil compartments, total amounts include both dissolved amounts in the pore water and adsorbed amounts (if applicable) on the soil matrix. Process-related inputs (Table F-4) are by atmospheric deposition, primary mineral weathering (in soil compartments) and biological production (decomposition and mineralization). Process-related outputs are by drainage water discharge or biological removal (uptake or immobilization). Unspecified sources and sinks of each ion are also available in the model. These may be used to simulate processes or perturbations not explicitly represented in the model (such as experimental additions of ions, losses of ions resulting from land use changes, etc.). At each time step during model simulation, inputs and outputs are added or subtracted from each compartment, new total amounts are calculated, and the equilibrium equations are solved subject to the constraint of ionic balance (Table F-1) to derive an estimate of the concentrations of the state variables (Table F-2) for that time step.

Nitrogen Immobilization Equations

Concern was expressed more than a decade ago about the possible adverse effects of atmospheric deposition of nitrogen compounds on soils, forests and waters. There is now

Table F-4. Inputs to the MAGIC model.

Input Fluxes and Conditions   (functions of time that must be specified)

Conditions are annual averages (monthly averages are specified for seasonal simulations)

Temperature (^{o}C), Carbon Dioxide (atm), Organic Acid (mol m^{-3}):   TEMP, P_{CO2}, $(OA)_{TOT}$

[CO_2 partial pressure and Organic Acid concentration control the weak inorganic and organic carbon buffers]

Fluxes are annual values (monthly fractions of annual fluxes are specified for seasonal simulations)

Catchment Discharge (m yr^{-1}) and Flow Fractions: Q, F_1, F_2, F_3

[Flow fractions specify the pathway of water flux through the modelled system and can vary seasonally]

Atmospheric Deposition (eq m^{-2} yr^{-1}): AD_{Ca}, AD_{Mg}, AD_{Na}, AD_K, AD_{NH4}, AD_{SO4}, AD_{Cl}, AD_{NO3}, AD_F

[Deposition is specified as the product of precipitation concentrations and amount, scaled by a dry deposition factor]

Sources and Sinks of Ions (eq m^{-2} yr^{-1}): SS_{Ca}, SS_{Mg}, SS_{Na}, SS_K, SS_{NH4}, SS_{SO4}, SS_{Cl}, SS_{NO3}, SS_F

[Sources and sinks are distinct and represent processes, inputs or outputs not explicitly included in the model]

The flow fractions determine atmospheric deposition fluxes into each soil and surface water compartment.
Other fluxes and conditions must be specified separately for each model compartment (if appropriate).

Initial Values

Initial values of these state variables must be specified for each model compartment (if appropriate)

Cation and Anion Concentrations (mol m^{-3}): (Ca^{2+}), (Mg^{2+}), (Na^+), (K^+), (NH_4^+), (SO_4^{2-}), (Cl^-), (NO_3^-), (F^-)

Exchangeable Ions (fraction): E_{Ca}, E_{Mg}, E_{Na}, E_K

evidence that some forests in Europe and North America are becoming nitrogen saturated, leading to enhanced nitrate leaching in drainage waters (e.g., Emmett et al.1993, Stoddard 1994, Dise and Wright 1995). Recent Experimental results from the NITREX Project (Wright and van Breemen 1995, Gundersen et al. 1998, Emmett et al. 1998) have provided insights into the controls on nitrogen cycling and have enabled the development of empirical models that relate nitrogen retention to the carbon and nitrogen characteristics of soil organic matter. It is important to incorporate this new process level understanding into dynamic models of acidification responses.

   There were no process-based mechanisms for nitrogen retention in soils in the original version of MAGIC. Ferrier et al. (1995) and Jenkins et al. (1997) modified MAGIC to produce a new coupled sulfur and nitrogen model (MAGIC-WAND) to address concerns over the interaction of sulfur and nitrogen deposition on soil and surface water acidification. MAGIC-WAND used many of the same processes included in the latest version of MAGIC but did not introduce an internal pool of stored nitrogen in the soil compartments. All of the nitrogen processes in MAGIC-WAND were rate-based and there was no internal state variable that could change the rates as nitrogen accumulated in the simulated systems (no feedback). Cosby et al. (1997) and Emmett et al. (1997) constructed a model (MERLIN) to deal explicitly with nitrogen dynamics in soils. The MERLIN model was based on both rates and internal pools and proved more capable of simulating nitrogen dynamics. However, MERLIN did not simulate the acid-base processes. The nitrogen dynamics included in the current version of MAGIC are based conceptually on the empirical model described by Gundersen et al. (1998) (see also Tietema and Beier 1995, Emmett et al. 1995). The mathematical formulation and process representations of

the nitrogen dynamics in the current version of MAGIC (Cosby et al. 2001) derive from a simplification of the structure of the MERLIN model.

Even though the current version of MAGIC has the capability to simulate dynamic nitrogen changes, these dynamics can be turned off. In this case, simple sink and source terms for nitrogen species are used in MAGIC to simulate N retention and release. In the absence of direct evidence that the N dynamics of a catchment are changing, it is appropriate to use the simple sink/source representation. For nitrate, this procedure specifies that retention (uptake) is a constant percentage loss of all inputs of nitrate (deposition, nitrification, etc). For ammonium, this procedure specifies that retention (uptake) is a constant percentage of all inputs of ammonium left over after nitrification has occurred. For the AQRV simulations presented in this report, nitrification of ammonium inputs was assumed to be 100%, and the % retention of the nitrate was calibrated based on observed input/output fluxes. This procedure assures that simulated and observed nitrate and ammonium agree very closely for the calibration period. The percentages of nitrification and nitrate retention were assumed to remain constant throughout the historical and future simulations.

Model Implementation

Atmospheric deposition and net uptake-release fluxes for the base cations and strong acid anions are required as inputs to the model. These inputs are generally assumed to be uniform over the catchment. Atmospheric fluxes are calculated from concentrations of the ions in precipitation and the rainfall volume into the watershed. The atmospheric fluxes of the ions must be corrected for dry deposition of gas, particulates and aerosols and for inputs in cloud/fog water. An estimate of the streamflow volume must also be provided to the model. In general, the model is implemented using average hydrologic conditions and meteorological conditions in annual or seasonal simulations. Mean annual or mean monthly deposition, precipitation and streamflow are used to drive the model. The model is not designed to provide temporal resolution greater than monthly. Most simulations are based on annual average conditions. Values for soil and streamwater temperature, partial pressure of carbon dioxide in the soil and streamwater, and organic acid concentrations in soilwater and streamwater must also be provided.

As implemented for this project, MAGIC is a two-compartment representation of each watershed. Atmospheric deposition enters the soil compartment and the equilibrium equations are used to calculate soil water chemistry. The water is then routed to the stream compartment, and the appropriate equilibrium equations are reapplied to calculate streamwater chemistry.

Once initial conditions (initial values of variables in the equilibrium equations) have been established, the equilibrium equations are solved for soil water and streamwater concentrations of the remaining variables. These concentrations are used to calculate the streamwater output fluxes of the model for the first time step. The mass balance equations are (numerically) integrated over the time step, providing new values for the total amounts of base cations and strong acid anions in the system. These in turn are used to calculate new values of the remaining variables and new streamwater fluxes. The output from MAGIC is thus a time trace for all major chemical constituents for the period of time chosen for the integration.

Model Calibration Procedure

The aggregated nature of the model requires that it be calibrated to observed data from a watershed before it can be used to examine potential system response. Calibration is achieved by setting the values of certain parameters within the model which can be directly measured or observed in the system of interest (called "fixed" parameters). The model is then run (using

observed atmospheric and hydrologic inputs) and the output (streamwater and soil chemical variables, called "criterion" variables) are compared to observed values of these variables. If the observed and simulated values differ, the values of another set of parameters in the model (called "optimized" parameters) are adjusted to improve the fit. After a number of iterations, the simulated-minus-observed values of the criterion variables usually converge to zero (within some specified tolerance). The model is then considered calibrated. If new assumptions (or values) for any of the fixed variables or inputs to the model are subsequently adopted, the model must be re-calibrated by re-adjusting the optimized parameters until the simulated-minus-observed values of the criterion variables again fall within the specified tolerance.

Because the estimates of the fixed parameters and deposition inputs are subject to uncertainties, a "fuzzy" optimization procedure can be implemented for calibrating the model. The fuzzy optimization procedure consists of multiple calibrations of each watershed using random values of the fixed parameters drawn from the observed possible range of values, and random values of deposition from the range of model estimates. Each of the multiple calibrations begins with (1) a random selection of values of fixed parameters and deposition, and (2) a random selection of the starting values of the adjustable parameters. The adjustable parameters are then optimized using the Rosenbrock (1960) algorithm to achieve a minimum error fit to the target variables. This procedure is undertaken ten times for each stream. The final calibrated model is represented by the ensemble of parameter values and variable values of the successful calibrations.

Calibrations are based on volume-weighted mean annual fluxes for a given period of observation. The length of the period of observation used for calibration is variable, but model output will be more reliable if the annual flux estimates used in calibration are based on a number of years rather than just one year. There is considerable year-to-year variability in atmospheric deposition and catchment runoff. Averaging over a number of years reduces the likelihood that an "outlier" year (very dry, etc.) constitutes the primary data on which model forecasts are based. On the other hand, averaging over too long a period may remove important trends in the data that need to be simulated by the model. For this study, the model was calibrated using five-year average values of deposition and five years of streamwater data.

The model results presented in this report are based on the median values of the simulated water quality variables from the multiple calibrations of each site. The use of median values for each stream helps to assure that the simulated responses are neither over- nor underestimates, but approximate the most likely behavior of each stream (given the assumptions inherent in the model and the data used to constrain and calibrate the model). The uncertainty analyses make use of the maximum and minimum simulated values from the multiple calibrations for each site to calculate uncertainty "widths" (or confidence intervals) around the median simulated values.

Comments on Model Applicability

The MAGIC model of acidification is a model that has been extensively subjected to the process of testing and confirmation over a 15-year period and thousands of applications. MAGIC has been used in scientific studies, as a tool in establishing management practices, and as an aid in making policy decisions regarding controls on emissions and deposition. Overall, the model has proven to be robust, reliable, and useful in all of these activities. The longevity and utility of MAGIC results as much from the philosophical approach to its formulation (empirically-based, compatible with readily available data, technically easy to implement, and capable of being tested), as from the soundness of the hydrobiogeochemical concepts and understanding on which the model is based. The success of this conceptual approach in the

qualitative and quantitative description of acidification responses of ecosystems suggests that it is also an appropriate tool for examining recovery responses as well.

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